



## Short communication

## Cell energy density and electrolyte/sulfur ratio in Li–S cells



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## HIGHLIGHTS

- Li–S cells usually have an excess of electrolyte and Li to improve the performance.
- The cell energy density drastically depends on the added electrolyte amount.
- Only small electrolyte/sulfur (E/S) ratios  $\leq 3:1$  enable high energy density cells.
- Pouch cells were created to examine electrode specific electrolyte/sulfur ratios.
- Low electrolyte/sulfur ratios decrease the sulfur utilization.

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## ABSTRACT

Li–S cells have high potential gravimetric cell energy densities between 200 and 600 Wh kg<sup>−1</sup>. To obtain a high cell energy density, the sulfur fraction in the electrode and the sulfur load per cm<sup>2</sup> electrode should be as high as possible next to a good electrochemical sulfur utilization. The quantity of electrolyte added to a cell is crucial for the latter, and an excess of electrolyte is generally beneficial for the electrochemical results. Existing publications on Li–S cells therefore use an excess of electrolyte leading to high electrolyte/sulfur (E/S in ml g<sup>−1</sup>) ratios as these enable high cycle numbers and good sulfur utilization. However, these studies do not take account of the high passive weight of the electrolyte. The high E/S ratios involved mean that the obtained cell energy density is below commercial lithium-ion cell level.

To emphasize the impact of the electrolyte on the cell energy density we calculated possible cell energy densities from material test cell experiments for various E/S ratios, sulfur and carbon loads. Furthermore small pouch cells with only a very small dead cell volume absorbing electrolyte are created to examine ideal E/S ratios for a specific electrode.

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## 1. Introduction

Li–S cells have significant potential as a next generation energy storage system with possible energy densities between 200 and 600 Wh kg<sup>−1</sup> on cell level. These energy densities are up to three times higher than those of commercialized Li-ion cells (150–250 Wh kg<sup>−1</sup>). For high energy densities on cell level the active material fraction and load should be as high as possible combined with ideally 1672 mAh g<sup>−1</sup> theoretical sulfur utilization. Over the last few years it has been observed that in particular the sulfur fraction in the electrodes could be improved from relatively low values between 20–50% and 60–80%, while tailored carbon materials even improved the electrochemical performance [1]. Nevertheless, the sulfur load per cm<sup>2</sup> electrode can still be seen as

too low, with values between 0.5 and 2.0 mg cm<sup>−2</sup>. To exploit the cost advantage of the cheap, abundant sulfur in comparison to commercialized Co and Ni containing electrodes, we believe that the sulfur load should be at least 3 mg cm<sup>2</sup> or preferably higher. Otherwise these Li–S cells may be even more expensive (\$ kWh<sup>−1</sup>) than commercialized systems because of their relatively low cell voltage [2]. Additionally the sulfur load has a significant effect on the achievable cycle number and possible Li-induced short-circuits. The higher the sulfur load, the more Li will be stripped and replated at the negative electrode, resulting in a much higher chance that Li dendrites will pierce through the separator. With high sulfur loads Li-induced shorts may even occur in the first 10 cycles [3]. For the same reasons high sulfur loads lead to the creation of a larger fresh Li surface during charge, when Li is redeposited at the negative electrode. For this fresh surface Li and electrolyte are consumed to create a new SEI layer, the composition of which is described in Ref. [4] for ether based electrolytes. Consequently ether-based Li–S electrolytes cannot be seen as stable. In particular the

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dimethoxyethane (DME) fraction in DME:dioxolane (DIOX) electrolytes is depleted and the fraction of electrochemically active Li decreases [5]. As a result the system loses electrochemically active Li and electrolyte solvent, which therefore have to be added in excess when assembling the cell. This significantly decreases the possible cell energy density and explains why in the literature high cycle numbers above 1000 generally correspond to small sulfur loads, usually below  $1.0 \text{ mg cm}^{-2}$ .

- Sulfur load:  $0.8 \text{ mg cm}^{-2}$ , capacity per g sulfur at 1000th cycle:  $500 \text{ mAh g}^{-1}$ , capacity decay rate: 0.039% per cycle, electrode area:  $1.27 \text{ cm}^2$ , electrolyte amount:  $60 \text{ }\mu\text{l}$ , E/S:  $\sim 59/1$  [1].
- Sulfur load:  $0.4\text{--}0.6 \text{ mg cm}^{-2}$ , capacity per g sulfur at 1000th cycle:  $700 \text{ mAh g}^{-1}$  [6].
- Sulfur load:  $1.28 \text{ mol l}^{-1}$  electrolyte, capacity per g sulfur at 1000th cycle:  $600 \text{ mAh g}^{-1}$  [7].

Furthermore important information which significantly affect the cyclability of a Li–S cell, such as the quantity of electrolyte and the mass of Li electrode added, or the Li excess, are missing in almost every Li–S publication. We would like to shift the focus away from approaches that try to maximize the sulfur utilization or the long-term cycle stability without taking the passive weight of the electrolyte into account, as these have a low practical relevance.

We therefore used experimental material test cell results to calculate possible E/S ratios, still allowing high gravimetric cell energy densities and assembled pouch cells with defined sulfur load and electrolyte volume to experimentally determine ideal E/S ratios for the here used Kynol electrode.

## 2. Experimental

### 2.1. Calculation of energy densities on cell level with a binder-free vertical aligned CNT electrode

To evaluate the jelly roll energy densities for various E/S ratios, we used experimental results with binder-free CNT-coated GDL10AA from the company SGL Carbon as sulfur cathodes [2]. The electrode thickness depends on the CNT coating load and is between 300 and  $700 \text{ }\mu\text{m}$  before assembly. In the test cells the electrodes are compressed to a thickness of  $250\text{--}400 \text{ }\mu\text{m}$  by a stainless steel spring with a force of approximately  $10 \text{ kg cm}^{-2}$ . The binder-free CNT electrodes can work with sulfur loads between  $0.5$  and  $20.0 \text{ mg cm}^{-2}$  electrode and show capacities between 800 and  $1000 \text{ mAh g}^{-1}$  sulfur ( $\text{mAh g}_\text{s}^{-1}$ ) for these sulfur loads at  $0.6 \text{ mA cm}^{-2}$  [2]. The electrolyte volume added to the test cells was constant at  $100 \text{ }\mu\text{l}$ , leading to effective experimental E/S ratios between 5 and 20. The estimated dead volume of the test cells that had to be filled with electrolyte was around  $20 \text{ }\mu\text{l}$ .

For the energy density calculations we used the following data:

- Sulfur cathode mass:  $\text{S}_8$  load + CNT load + carbon current collector (GDL10AA) +  $6 \text{ }\mu\text{m}$  Al current collector (for single side coated electrode).
- Lithium metal anode: Li load without excess of Li (Li capacity matching  $\text{S}_8$  cathode capacity) +  $5 \text{ }\mu\text{m}$  Cu current collector (for single side coated electrode).
- Separator with  $1.0 \text{ mg cm}^{-2}$  and electrolyte with  $1.0 \text{ mg }\mu\text{l}^{-1}$  ( $1 \text{ g ml}^{-1}$ ).
- We did not include the weight of the housing and the tabs because this passive weight fraction greatly depends on cell type and size. To obtain the cell energy density the calculated jelly roll energy density values could be multiplied with  $0.75\text{--}0.95$ . We suggest that an electric vehicle pouch cell with  $\sim 60 \text{ Ah}$

might be close to 0.95. Cells with a higher relative housing weight should be close to 0.75.

- To obtain the energy densities on jelly roll level we divided the obtained capacity by the masses stated above, used various notional E/S ratios, and multiplied the result by an average cell voltage of  $2.1 \text{ V}$ .

### 2.2. Pouch cell assembly using a Kynol 5092-20 electrode

The Li–S pouch cells were created by infiltrating  $\text{S}_8$  in Kynol 5092-20 electrode (weight:  $\sim 13.5 \text{ mg cm}^{-2}$ , thickness:  $\sim 550 \text{ }\mu\text{m}$ , electrode surface:  $\sim 1800 \text{ m}^2 \text{ g}^{-1}$ ). The sulfur load was  $6.6 \text{ mg cm}^{-2}$  and the sulfur electrode fraction was 33%. The Kynol- $\text{S}_8$  and the Li electrode (Sigma Aldrich, 99.9%) were cut in a rectangular shape ( $5 \times 3 \text{ cm}$ ). Beforehand the Li was scraped with a ceramic knife to remove undesired surface layers and pressed through a calendar to obtain a homogenous and reproducible surface. The Li thickness was around  $180 \text{ }\mu\text{m}$  (Li excess of 234%, referred to the theoretical  $\text{S}_8$  capacity). The Kynol- $\text{S}_8$  electrode was conductively glued to a  $12 \text{ }\mu\text{m}$  thick Al current collector with an electrodag and the Li electrode was pressed onto a  $10 \text{ }\mu\text{m}$  Cu current collector using a small calendar. A Ni/Cu tab was welded to the copper current collector and an Al tab was welded to the Al current collector using a Branson ultrasonic welding device. As a separator a Celgard ECT2015 (size  $6 \times 4 \text{ cm}$ ) was used and directly laminated onto the electrodes to obtain a stack. The stack was placed in the middle between two pouch foils (size  $8 \times 5 \text{ cm}$ ) and the pouch foil was sealed with a vacuum sealing device. Before sealing the last edge of the cell we introduced a defined amount of  $0.7 \text{ M LiTFSI}$  in DME:DIOX ( $2:1, \text{ v:v}$ ) (BASF) +  $0.25 \text{ M LiNO}_3$  (ABCR 99.98%) with a water content below  $20 \text{ ppm}$  electrolyte. Unfortunately we discovered that  $5\text{--}30\%$  of the injected electrolyte evaporated out of the cell when the final sealing took place under vacuum. Since the aim of this work was to examine defined E/S ratios we developed a new method to guarantee that the injected electrolyte volume was equal to the final test cell electrolyte volume. We therefore inserted a polytetrafluoroethylene (PTFE) filled polyethylene (PE) tube into a silicone tube mounted to the pouch cells edge which worked as a kind of septum (Fig. 1a, b). This allowed us to inject the electrolyte when the pouch cell was completely sealed and evacuated. The projecting end with the silicone/PTFE/PE tube was cut away after a final sealing step (Fig. 1c).

The assembly of all test cells and pouch cells took place in an argon-filled glove box (MBraun) with an  $\text{O}_2$  and  $\text{H}_2\text{O}$  content below  $1 \text{ ppm}$ .

### 2.3. Electrochemical characterization

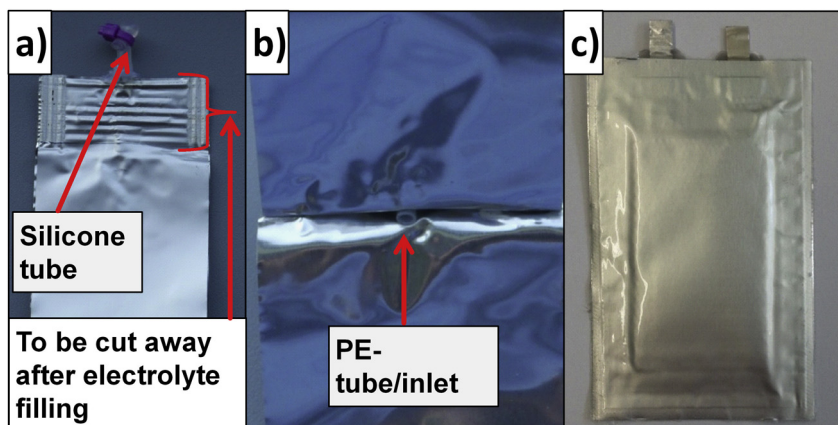
The binder-free CNT electrodes were cycled with  $0.5 \text{ mA}$  ( $0.64 \text{ mA cm}^{-2}$ ) between  $1.8$  and  $2.8 \text{ V}$ . The cycle station used was a Basytec CTS-LAB system.

The Li–S pouch cells with Kynol electrode were cycled with  $10 \text{ mA}$  ( $0.67 \text{ mA cm}^{-2}$  or  $0.1 \text{ A g}^{-1}$  sulfur or C/16) between  $1.8$  and  $2.8 \text{ V}$ .

## 3. Results and discussion

### 3.1. Calculated gravimetric jelly roll energy densities based on binder-free vertical aligned CNT electrode – E/S ratio vs. specific energy density

Fig. 2 shows the calculated jelly roll energy densities with binder-free, vertically aligned CNT- $\text{S}_8$  cathodes for various  $\text{S}_8$  loads, CNT loads and different E/S ratios. The CNTs provide a high



**Fig. 1.** Pouch cell electrolyte filling device: a) septum like silicon tube with inserted PE and PTFE tube, welded to the pouch foil, b) PE tube as electrolyte inlet inside the pouch cell, c) assembled and electrolyte filled pouch cell. The projecting end with the septum was cut away.

conductive framework and increase the electrode surface. Without a CNT coating (CNT load:  $0 \text{ mg cm}^{-2}$ ) the energy densities are low ( $80\text{--}160 \text{ Wh kg}^{-1}$ ) depending on the E/S ratio. The electrode surface of the basic substrate (no CNT coating) is not sufficient to provide enough reaction sites for the sulfur and  $\text{Li}_2\text{S}$ . By applying a CNT coating the possible energy densities rise to values between  $150$  and  $400 \text{ Wh kg}^{-1}$ . Especially with high CNT coating loads high sulfur loads are necessary to compensate the carbon's passive weight and to obtain energy densities above  $300 \text{ Wh kg}^{-1}$ . Additionally it can be clearly seen that the different E/S ratios have a dominant effect on the jelly roll energy density that can be obtained. E/S ratios of 5/1 or 4/1 deliver energy densities between  $150$  and  $300 \text{ Wh kg}^{-1}$ . Such Li–S cells therefore only have an energy density comparable to state-of-the-art Li-ion high-energy cells which can additionally provide several thousand stable cycles and which are also likely to be much safer and easier to produce than Li–S cells. As a result there would never be a market for such Li–S cells. Only E/S ratios of around 3/1 or 2/1 can significantly improve the cell energy density above state-of-the-art level with values up to  $400 \text{ Wh kg}^{-1}$ . Energy densities of around  $500 \text{ Wh kg}^{-1}$  could be achieved with an E/S ratio of 2/1 and a very high sulfur utilization of

$1300 \text{ mAh g}_\text{S}$  which we obtained only at moderate currents with these sulfur loads (but only with a higher amount of electrolyte). A further but very costly way to improve the energy density is to reduce the weight of the current collectors below the typical values through for example sputtering methods [8]. Additionally the weight of the Li metal anode could be reduced by using a negative electrode with no excess of Li. Thin Li anodes could for example be created by evaporation methods [8]. Nevertheless, one should keep in mind that there is still the continuous electrolyte and active Li consuming reaction which enforces the addition of a Li excess and an electrolyte excess in the cell. Only concepts with protected Li metal anodes combined with uniaxial pressure on the electrode stack might reduce this effect, at least as long this protection is intact [5,8].

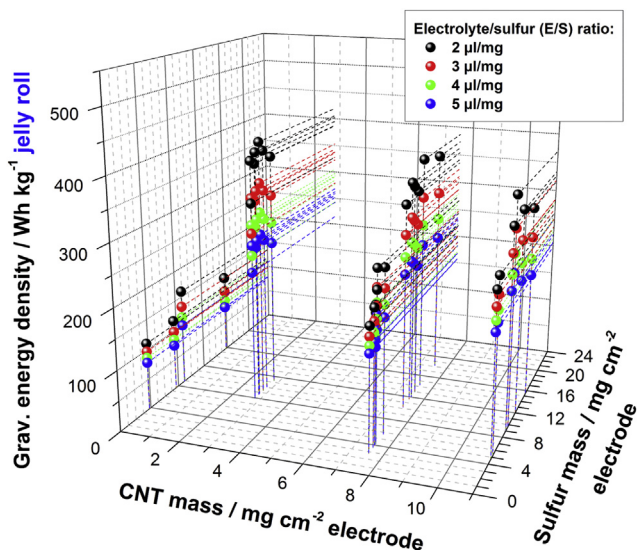
It is interesting to note that current literature concerning the optimization of E/S focuses completely on maximizing the sulfur utilization and on the cyclability but not on the cell energy density.

- Choi et al. examined various electrolyte volumes ( $4, 12, 30 \mu\text{l}$ ) for a S cathode with  $0.95 \text{ cm}^2$ ,  $20 \mu\text{m}$  thickness and a sulfur load of maybe up to  $1.2 \text{ mg}$ . At cycle 20 the cell with  $12 \mu\text{l}$  showed the highest capacities ( $500 \text{ mAh g}_\text{S}^{-1}$ ) [9].
- Zhang examined the disproportion reaction of polysulfides in electrolytes and scanned E/S ratios of 13.3, 10 and 6.5. The S cathode ( $77\% \text{ S}$ ) with  $1.27 \text{ cm}^2$  had a sulfur load between  $2.0$  and  $3.3 \text{ mg cm}^{-2}$ . The capacities were most stable at an E/S ratio of 10:1 with  $800 \text{ mAh g}^{-1}$  after 100 cycles [10].
- Cheng et al. examined various E/S ratios (S electrode area:  $1.32 \text{ cm}^2$ , thickness:  $10\text{--}15 \mu\text{m}$ ) with S loads of  $0.34, 0.51, 1.12, 2.58 \text{ mol l}^{-1}$  electrolyte (possible E/S ratios  $\sim 92, 61, 28, 12$ ). S concentrations of  $1.12 \text{ mol l}^{-1}$  delivered the highest discharge capacities of  $1100 \text{ mAh g}^{-1}$  for the second cycle at  $0.1\text{C}$  [7].

Consequently high cell level energy densities will not be possible with these E/S ratios suggested to be optimal for high sulfur utilization.

### 3.2. Pouch cell experiments with Kynol 5092-20 electrode and E/S ratios between 3/1 and 8/1 – E/S ratio vs. capacity

To maximize the cell energy density the electrolyte volume in the cell should be as low as possible and the sulfur utilization should be as high as possible. The pouch cell setup proposed here is suitable for this test, because the evacuated pouch cell only has a



**Fig. 2.** Second cycle jelly roll energy density of a CNT coated carbon structure as a function of the S and CNT load with E/S ratios between 2 and  $5 \mu\text{l mg}^{-1}$ .



small dead volume and the injected electrolyte should be almost completely in the electrode stack.

Fig. 3 shows corresponding voltage/capacity plots with Kynol-S<sub>8</sub> electrode at various E/S for the first cycle and Fig. 4 for the 7th cycle. For high E/S above 7/1 acceptable capacities of around 1000 mAh g<sup>-1</sup> (~350 mAh g<sup>-1</sup> electrode) could be obtained. Lower E/S ratios lead to greatly reduced capacities with poor 50 mAh g<sup>-1</sup> at an E/S of 3/1. Regarding the capacity for the electrode + electrolyte (compare Fig. 3 and Fig. 4) those are between 30 and 100 mAh g<sup>-1</sup> for the first cycle and only 10–90 mAh g<sup>-1</sup> for the 7th cycle, leading to poor cell energy densities below 200 Wh kg<sup>-1</sup>. The capacity fade in the direction of smaller E/S can be explained by the Li–S reaction mechanism. At the voltage minimum between the upper and lower discharge plateau the electrolyte (and the overall cell-) resistance reach a maximum because the polysulfide concentration in (and consequently the viscosity of) the electrolyte is highest during discharge [11]. If the quantity of electrolyte added to the cell is too low the viscosity becomes critical and the discharge stops before the second plateau starts (compare E/S: 3/1 and 4/1) leading to small total capacities. Next to these electrochemical restrictions enforcing a minimum E/S the sulfur cathode itself should be designed to be operable with small E/S ratios. This is not the case with the Kynol-S<sub>8</sub> electrode discussed here which only shows acceptable results at E/S above 7/1. Additionally the sulfur fraction (33%) was too low to obtain a high energy cell but the focus in this manuscript was the examination of various E/S ratios.

It is likely that many sulfur cathodes introduced in the past few years may not be suitable to yield high cell energy densities, because they were only examined with an electrolyte excess in material test cells, with the aim of achieving good cyclability and sulfur utilization. It might be more reasonable to not only maximize the sulfur utilization and sulfur fraction in the electrode but also to maximize the capacity for the complete electrode weight including current collector and electrolyte. A real high energy cell might have capacities of at least 200 mAh g<sup>-1</sup> (S<sub>8</sub> electrode + electrolyte). Also energy density calculations based on a very small E/S < 1:1 with extrapolation of electrochemical results obtained from a 0.8 mg cm<sup>-2</sup> sulfur load electrode to a cell with 6 mg cm<sup>-2</sup> sulfur load yielding initial 500 Wh kg<sup>-1</sup> might be too optimistic [1].

Commercialized Li–S cells for the niche market of drones obtain their high energy density of 350 Wh kg<sup>-1</sup> [8] because of their

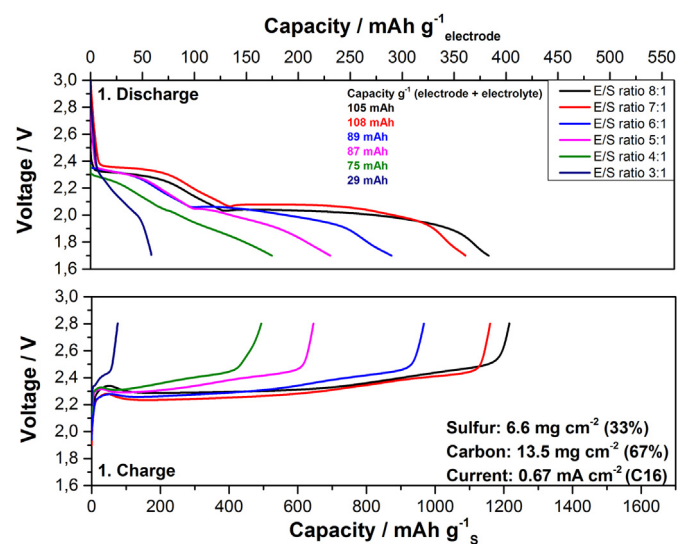


Fig. 3. Li–S pouch cell first cycle voltage/capacity plot for various electrolyte/sulfur (E/S) ratios.

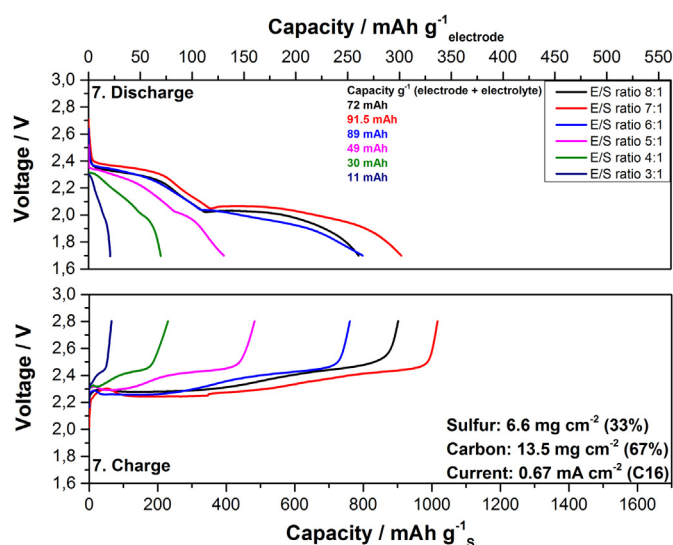


Fig. 4. Li–S pouch cell 7th cycle voltage/capacity plot for various electrolyte/sulfur (E/S) ratios.

comparably low E/S of ~3.2/1 with a capacity of 1007 mAh g<sup>-1</sup> in multi-layer stack cells [12]. Multi-layer stack cells can further reduce the E/S by a small amount, at least with the Kynol electrode used here. Nevertheless even multi-layer electrode stack cells will not reduce the E/S ratio to commercially interesting values, when the same electrode already demanded high E/S ratios in single layer assembly. Therefore additional strategies are needed to obtain low E/S ratios combined with good sulfur utilization.

Since the discharge capacity reaction mechanism can be stopped by electrolyte viscosity/resistance one strategy for lower E/S ratios might be to reduce the drained power exactly when the electrolyte resistance reaches its maximum or to reduce the discharge cut-off voltage. When the electrolyte resistance drops during the lower discharge plateau the power might be gradually increased again. Nevertheless, it is questionable whether typical applications or customers could accept this power restriction.

A more promising method could be the encapsulation of sulfur inside the cathode preventing polysulfide dissolution out of the catholyte, although the original target of this method was to prevent the shuttle mechanism. Ji et al. published that it was possible to reduce the polysulfide dissolution out of the catholyte by trapping the sulfur inside a CMK-3 carbon nanocage [13]. As a result the polysulfides must have been created locally inside the nanocages and only within the sulfur cathode. If the polysulfides don't dissolve out of the catholyte the electrolyte resistance might not become critical and high sulfur utilizations at low electrolyte volumes might still be possible.

A coating of the electrode with Nafion (or other polysulfide “blocking” materials), using Nafion as a binder [14] or coatings with polyethylene glycol [13] might also prevent polysulfide dissolution [14] out of the catholyte if the coating is homogenous and if there are no uncovered areas [15]. Even better might be sulfur cathodes in which the sulfur is covalently bonded to a composite, with polyacrylonitrile (PAN)-S as the most popular cathode composite material. Here the S<sub>8</sub> does not dissolve or at least will dissolve very slowly and only in small concentrations. The reaction mechanism of PAN-S cells is not based on polysulfides and that's why carbonate based electrolytes with very low polysulfide solubility show better electrochemical results than ether based electrolytes with high polysulfide solubility [16]. Most likely the drawback of a comparably small active material fraction and lower average discharge cell

voltage of a PAN-S–Li cell ( $\sim 1.7$  V) could be compensated by good capacities of  $>400$  mAh  $\text{g}_{\text{electrode}}^{-1}$  [17] and a possibly lower amount of electrolyte needed in the cell.

Last but not least the electrolyte itself could be designed to reduce polysulfide dissolution. This could be done by reducing the fraction of solvents with high polysulfide solubility (e.g. ethers) and by substituting them with substances with lower polysulfide viscosity (e.g. ionic liquids, sulfones) [9,11] or simply by increasing the conductive salt [18,19] or  $\text{LiNO}_3$  concentration. Song et al. demonstrated high power performance and high coulombic efficiencies with an electrolyte consisting of 50 vol% ionic liquid and 50 vol% ether with comparably high 0.5 M  $\text{LiNO}_3$  [1]. Although the electrode's sulfur load was moderate ( $0.8 \text{ mg cm}^{-2}$ ) these results might show that high power performance and sulfur utilization combined with lower electrolyte polysulfide solubility is possible, contradicting the assumptions of Ref. [5]. Still it is common knowledge that cells with elemental sulfur in the cathode aren't operable in electrolytes with very low or no polysulfide solubility, like carbonates [16].

#### 4. Conclusion

Jelly roll energy density calculations were made with a focus on the electrolyte/sulfur ratio (E/S in  $\text{ml g}^{-1}$ ). Only an E/S ratio of  $\sim 3/1$  or lower may enable high energy density cells. Unfortunately the sulfur utilization is in general significantly reduced at low E/S, here examined in small pouch cells with almost no dead volume for the electrolyte. Some methods of reducing the E/S ratio could be the use of special designed electrolytes with optimized polysulfide dissolution properties, sulfur cathodes with polysulfide retention by special binders (e.g. Nafion), encapsulated sulfur or PAN-S type electrodes.

So far the weight of the electrolyte has not been taken into account in many publications, in which the focus was only set on high sulfur utilization and high cycle numbers, which are both obtained through an excess of electrolyte and an excess of Li. To evaluate the Li–S cell performance it would be very helpful if future literature contains these important parameters next to the  $\text{S}_8$  electrode fraction, the  $\text{S}_8$  load, the applied current related to the electrode area + C rate, the capacity for the complete electrode and the capacity for the complete electrode including the electrolyte's weight.

Ideally the sulfur cathode should be designed to be operable with a small amount of electrolyte right from the start of development and the capacity should be maximized including the weight of the complete  $\text{S}_8$  cathode and electrolyte. Still such a high

energy electrode will suffer very low cycle numbers because of electrolyte depletion with consequent cell dry out. This depletion could be stopped if the contact of the liquid electrolyte with the Li anode is prevented by a reliable and enduring  $\text{Li}^+$  conductive protection layer. Another possible way to prevent the depletion could be an electrolyte that is extremely stable towards Li or reliable strategies or cell assemblies which guarantee that fresh deposited Li is plated below the existing Li-SEI without creating a new SEI, consuming Li and electrolyte (e.g. through dendrites).

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